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STANFORD UNIV CALIF CENTER FOR MATERIALS RESEARCH  
PREPARATION AND CHARACTERIZATION OF SINGLE CRYSTALS AND EPITAXIAL--ETC(U)  
OCT 79 T H GEBALLE , R S FEIGELSON , D ELWELL N00014-78-C-0489

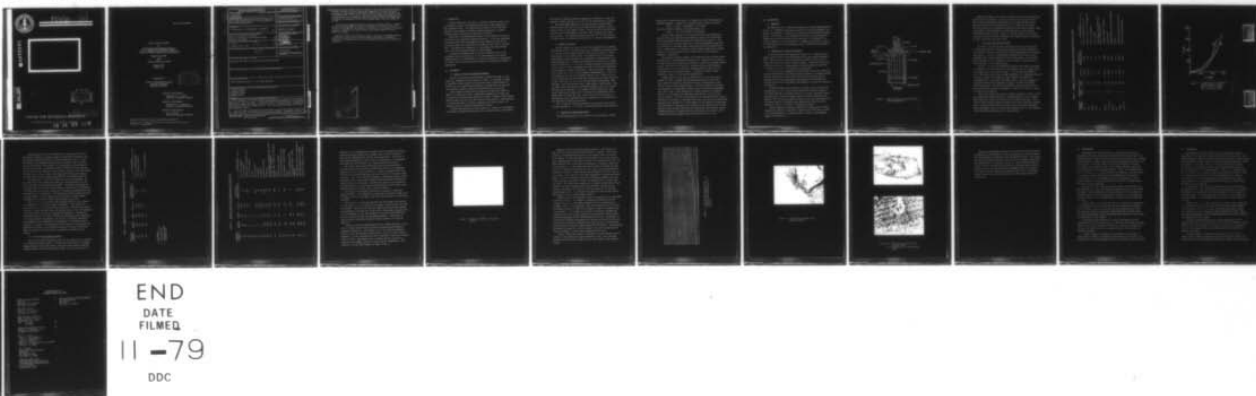
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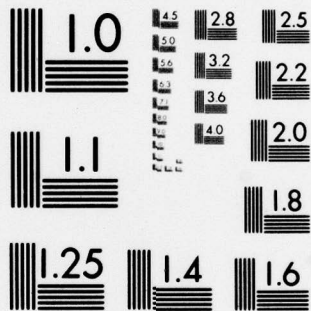
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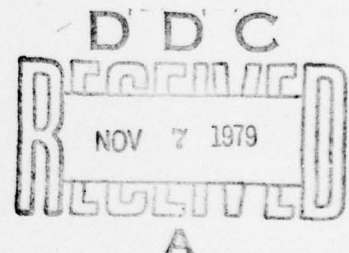
Report #243-026-001

Annual Technical Report  
on  
PREPARATION AND CHARACTERIZATION OF  
SINGLE CRYSTALS AND EPITAXIAL LAYERS OF  
SILICON CARBIDE BY MOLTEN SALT ELECTROLYSIS

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The synthesis of silicon carbide by electrolysis of molten salts has been achieved for the first time. Two systems have been investigated, one involving $K_2SiF_6$ and $Li_2CO_3$ dissolved in a $KF/LiF$ eutectic, the other being a combination of $Na_2CO_3$ and $SiO_2$ with $NaBO_3$ and $LiF$ . The latter system has given much more reproducible results.  In both cases, electrolysis has proceeded at about $750^\circ C$ which is very low in comparison with the melting point of silicon carbide. Synthesis of $SiC$ at			

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20.→ temperatures below 1000°C does not appear to have been previously reported. Possibly because of the low deposition temperature, it has been found necessary to use deposition potentials which are appreciably higher than the minimum value. This use of relatively high deposition potentials and corresponding current densities leads to irregular growth morphology and to deposition of metastable 2H and 33R polytypes rather than the stable 6H or 15R.

The SiC is co-deposited with an excess of amorphous carbon. Changes in melt composition ~~are~~ to reduce the carbonate to silicate ratio are necessary to eliminate this excess. In addition, it is planned to increase the melt temperature in order to reduce the current density at which deposition occurs.

Initial deposits are relatively impure, the major contaminants being constituents of the inconel furnace lining. These may be removed by changing the atmosphere tube or by the use of a new furnace now under construction.

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## I. INTRODUCTION

Silicon carbide is a material of very great interest since it can in principle be used in semiconducting devices at high temperatures and radiation levels. Its application in devices to date has been limited by the problems involved in growing materials of suitable size and quality and with the appropriate structure.

Molten salt electrodeposition offers a novel approach to the preparation of this relatively difficult material. It has the advantages that deposition occurs isothermally and the deposition rate may be controlled simply and accurately by varying the cell current or potential. The deposition temperature is low compared with the melting point, and the equipment required is fairly simple.

Although electrodeposition of silicon carbide has not, to our knowledge, been achieved prior to this investigation, this method appeared worthy of investigation as a means of making SiC, particularly in view of the problems encountered using more conventional methods of preparation.

## II. BACKGROUND

### A. Crystal Growth by Alternative Methods

Silicon carbide melts incongruently at 2830°C but tends to lose silicon at temperatures well below this value. In principle it might be possible to grow crystals from the melt under a high pressure of silicon, but the equilibrium Si pressure is apparently very high and the technical problems of growth from the melt are very severe.

Vapor growth has been used at temperatures from about 1000°C to 2500°C. In some cases direct sublimation-condensation is used, the so-called Lely process being employed at 2500°C to prepare rather impure crystals which are used for some electronic applications. More generally a transporting agent is used for synthesis and crystal growth, for example, SiCl<sub>4</sub> for silicon and methane for carbon.

Growth from solution has been reported by a number of investigators, the solvents including transition metals, rare earth metals and silicon.



The latter is normally preferred although the solubility is only one percent at 2150°, falling to  $5 \times 10^{-5}$  at the melting point of silicon.

The latest ORNL Directory of Crystal Growth activities (ORNL-RMIC-14, March 1979) lists only four laboratories engaged on crystal growth of SiC, two of these in Japan. Of the two which give the method used, one uses sublimation, the other vapor transport and liquid phase epitaxy. The largest crystals listed are 10 X 10 X 0.5 mm and are grown using the sublimation method by D. R. Barrett (Westinghouse).

#### B. Crystal Structure

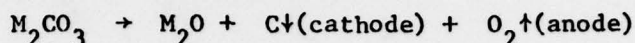
Silicon carbide can occur in cubic (C) hexagonal (H) or rhombohedral (R) structures. The basic unit is a tetrahedron consisting either of a silicon atom covalently bonded to four carbon atoms or a carbon atom bonded to four silicon atoms. The complexity of its structure arises since successive layers can be parallel or antiparallel and it is the combination of parallel and antiparallel layers that is responsible for polytypism. If 'p' and 'a' denote parallel and antiparallel layers, the most stable polytypes are 6H ( $\alpha$ -) and 15R with respective layer sequences (pppaaa) and (pppaa)<sub>3</sub>. The 33R polytype, referred to later in the report, has a layer sequence (pppaaapppaa)<sub>3</sub>. A total of 140 polytypes are said to be possible (Tairov et al., 1977), but the common production processes yield about 85 percent of 6H and 12 percent of 15R. The cubic (3C or  $\beta$ -) form is metastable (Knippenberg, 1963) although it has been produced over a wide range of temperatures. Many polytypes share the same X-ray diffraction peaks so that firm identification may be difficult. For example, 2H-SiC (Moissanite, space group P6<sub>3</sub>MC) has 12 peaks out of 24 listed on the ASTM Index card in common with the cubic ( $\beta$ ) form. Since the 2H and  $\beta$  were formed in combination in the experiment used for compilation of the index card, the intensities listed are uncertain.

The  $\beta$  form is considered optimum for electronic device applications although the  $\alpha$  is also a potentially useful device material.

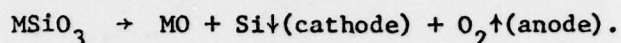
#### C. Principle of Electrodeposition

The electrodeposition of SiC requires the simultaneous cathodic

deposition of silicon and carbon at a temperature sufficiently high for compound formation. Carbon can be deposited from a molten carbonate:



and silicon from a silicate or fluorosilicate, e.g.,



Thermodynamic analyses of the various possible electrodeposition processes have been made and the temperature ranges over which alkali metal and alkaline earth carbonates and silicates will yield C and Si, respectively, have been predicted. These thermodynamic predictions are, however, not reliable since irreversible electrode processes may occur. Additionally, in binary or ternary systems there may be complex formation which changes the order of deposition of the competing elements or compounds.

In principle, silicon carbide can be deposited from a binary carbonate/silicate or carbonate/fluorosilicate melt. Additions of a ternary or even a quaternary phase may be necessary to lower the liquidus temperature or the viscosity of the melt. Alkali halides are particularly favored since they are effective at breaking silicate chains and are themselves electrochemically stable. In general, however, stable deposition requires a high solute concentration.

Single phase SiC will only be produced if the Si:C ratio in the deposit is unity, although the reaction between silicon and carbon atoms would be expected to influence the local concentration of both Si and C atoms at the cathode surface. The first problem in achieving the deposition of single phase material of good crystalline morphology (as a first state in the preparation of single crystals or epitaxial layers) is to determine the conditions under which a 1:1 Si:C ratio can be achieved. This ratio will depend on the concentrations of fluorosilicate (or silicate) to carbonate in the melt and also on the deposition potential and, probably to a lesser degree, on the deposition temperature. The morphology of the deposit is controlled by the potential (or current density, which directly determines the deposition rate) and good crystallographic quality is normally obtained at potentials very close to the minimum deposition potential where the deposition rate is low.

### III. EXPERIMENTAL

#### A. Apparatus

The apparatus used in these investigations is shown diagrammatically in Fig. 1. A Kanthal-wound furnace encloses an inconel atmosphere tube which is fitted with a flange for the insertion of electrodes and thermocouple. The flange is also provided with fittings for evacuating the chamber and for introducing a flow of argon gas. A viewing port is used for insertion of the electrodes or a light bulb provides a source of illumination inside the atmosphere tube to facilitate positioning of the electrodes.

#### B. Deposition of Carbon and Silicon

It had been previously reported by Ingram et al. (1965) that elemental carbon could be electrodeposited from a pure lithium carbonate melt. This was confirmed by electrolysis at 740°C using a gold foil anode and cathode and vitreous carbon crucible. Deposition occurred at 1.70V, the current increasing during a 16 hour experiment from 66 mA to 146 mA, as the effective cathode area increased.

It was considered important to confirm that this carbon deposition process is substantially unaffected by the presence of an alkali halide solvent, since the presence of such materials in the bath finally selected for SiC electrodeposition was expected to be necessary to dissolve the Si-containing species and possibly to reduce the viscosity of the melt.

The LiF/KF eutectic was chosen as a solvent since it has the low melting point of 492°C and is less volatile than chloride eutectics. It suffers from the disadvantage that LiF is rather insoluble in water and acids and so adhering trances cannot be easily removed from the deposit. KF is extremely soluble in water but is very hygroscopic and the powder must be dehydrated before weighing and the melt must be exposed as little as possible to atmospheric moisture.

A melt containing equimolar quantities of  $\text{Li}_2\text{CO}_3$  and the LiF/KF eutectic was electrolyzed at 750°C. Deposition at 1.25C with a current of 6-11 mA resulted in a uniform coating of carbon on the immersed region of the gold foil.



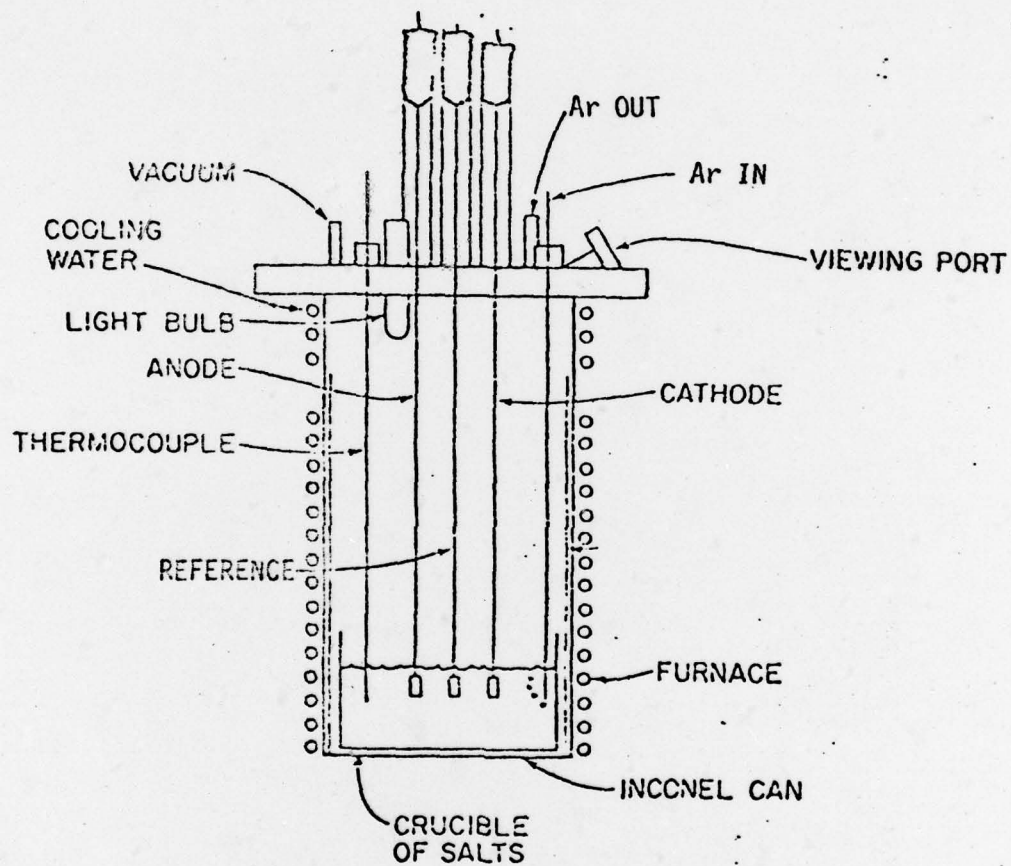


Figure 1. Apparatus used for electrodeposition (diagrammatic).

$K_2SiF_6$  was chosen as the source of silicon because of its relatively wide use for this purpose. It has been found in our laboratory that dense, coherent polycrystalline layers up to several mm thick can be deposited on silver foil cathodes (Rao et al., 1979) and that thin epitaxial layers can be deposited on single crystal silicon (Cohen, 1977) using  $K_2SiF_6$  dissolved either in LiF/KF eutectic or in the ternary LiF/NaF/KF eutectic "Flinak".  $K_2SiF_6$  is the most stable of the alkali fluorosilicates and the loss of material by volatilization from solution becomes significant only above 750°C.

### C. The System $K_2SiF_6/Li_2CO_3/LiF/KF$

In view of the relative ease with which carbon and silicon could be deposited separately from  $Li_2CO_3$  and  $K_2SiF_6$  respectively dissolved in the KF/LiF eutectic, initial studies were concentrated on this quaternary system. A total of 50 experiments (summarized in Table I) were performed, two of which yielded SiC in the 33R polytype. SiC was probably produced in other experiments, but problems of characterization did not permit a clear identification.

Plots of current versus deposition potential are useful in attempts to understand the deposition process and typical plots for  $Li_2CO_3$  alone and  $Li_2CO_3 + K_2SiF_6$  are shown in Fig. 2. In this case the anode was gold. The  $K_2SiF_6$  clearly has a marked influence on the deposition process although it cannot be assumed from this evidence that silicon is co-deposited with carbon from the binary solute. In fact, analysis of the deposit from a melt containing 1  $Li_2CO_3$ : 1 LiF/KF: 0.05  $K_2SiF_6$  showed only carbon. The ratio of carbonate to fluorosilicate in the melt was therefore reduced in attempts to achieve a 1:1 ratio of silicon to carbon in the deposit.

Since free silicon reacts quite strongly with gold at 750°C, silver was preferred as cathode material, although experiment 1 used niobium. This metal also reacts with silicon to form niobium silicides. Silver was the least reactive substrate studied at the above deposition temperatures. Vitreous carbon was used as the container material throughout these experiments since it is very inert against attack by the components of the salt bath and normally has a long lifetime.

TABLE I: SUMMARY OF ELECTRODEPOSITS USING LiF/KF EUTECTIC SOLVENT AT 750°C

Experiment Number	Concentrations (m/o)		P.D. (v)	Measurement Density (mA/cm <sup>2</sup> )	Observations
	K <sub>2</sub> SiF <sub>6</sub>	Li <sub>2</sub> CO <sub>3</sub>			
1-4	5	5	1.2-2.3	8-40	90% Si in deposit for V 1.9
5-9	5	10	1.2-2.0	6-29	Deposit only for V 1.8; excess Si
10-16	5	30	1.1-1.4	5-72	90-99% C in deposits
17-20	5	20	1.4	23	Excess carbon
21	5	20	1.6	32	First deposit of SiC(33R) with excess carbon and LiF
22-30	5	20	1.3-2.0	8-208	Li <sub>2</sub> SiO <sub>3</sub> at high V; excess C
31, 43, 44	10	20	1.5-2.0	9-16	Carbon excess
32-37	5	20	1.6	27-34	Reproducibility study; thin deposits
38	5	20	1.6	40	33R SiC
39-42	5	20	1.6-3.2	10-312	Li <sub>2</sub> SiO <sub>3</sub> at high V; some free Si
45-49, 51	5	20	1.6	35-44	Free Si with excess carbon



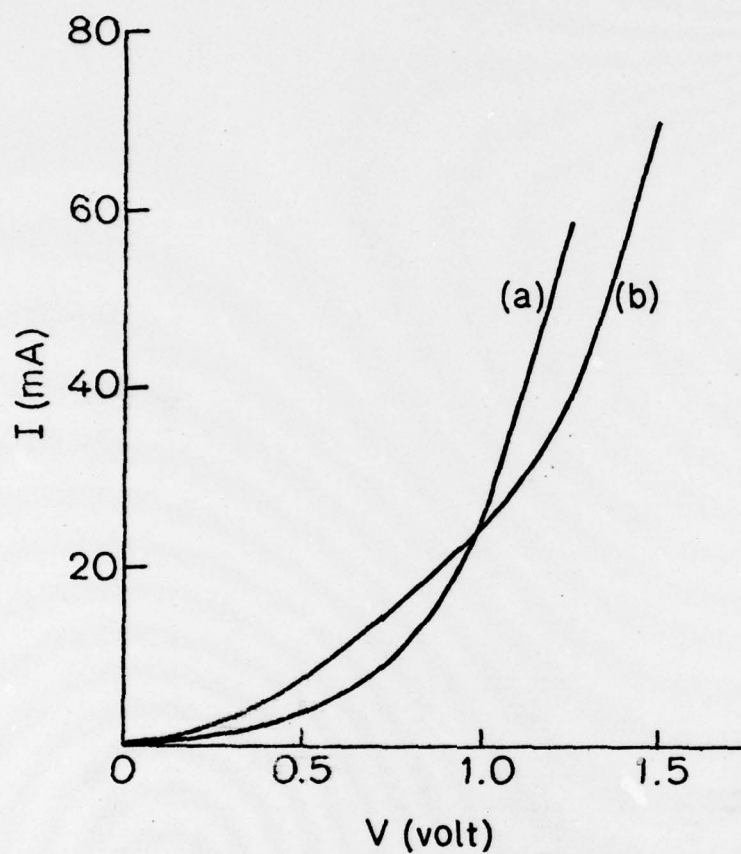


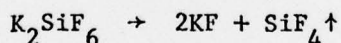
Figure 2. Voltammogram for solutions in LiF/KF eutectic at 750°C  
 (a) 1  $\text{Li}_2\text{CO}_3$  : 1 LiF/KF;  
 (b) 0.05  $\text{K}_2\text{SiF}_6$  added.

Plots of current versus the cathode-anode potential difference normally exhibit a single wave as shown in the example of Fig. 3. The minimum deposition potential, obtained by extrapolating the deposition current to intersect the V axis, is about 1.4V and varies quite slowly with the concentrations of  $\text{Li}_2\text{CO}_3$  and  $\text{K}_2\text{SiF}_6$ .

Analysis of the early deposits (1 to 16) was mainly by electron microprobe. Energy dispersion analysis is not sensitive to carbon and so may be used only to confirm the presence of silicon in the deposits and to correlate this with the grain structure as seen in the scanning electron microscope. Microprobe analysis for carbon using the crystal spectrometer was found to be quantitatively unreliable but was used as a semiquantitative indication of the presence of free or combined carbon.

Analysis of deposits from a melt containing 5 m/o  $\text{K}_2\text{SiF}_6$  and 5 m/o  $\text{Li}_2\text{CO}_3$  (experiments 1-4) indicated excess of silicon. Increase of the  $\text{Li}_2\text{CO}_3$  concentration to 10 m/o (experiments 5-9) also indicated silicon excess. However, further increase to 30 m/o  $\text{Li}_2\text{CO}_3$  (experiments 10-16) gave deposits with a large excess of carbon. The majority of subsequent experiments were therefore performed using a melt of composition 0.50 LiF; 0.50 KF; 0.05  $\text{K}_2\text{SiF}_6$ ; 0.20  $\text{Li}_2\text{CO}_3$ , although the  $\text{K}_2\text{SiF}_6$  concentration was increased to 0.10 for some depositions.

The Si:C ratio in the deposit is expected to depend on the melt composition, temperature and deposition potential (versus platinum). The maximum temperature at which this bath could be operated is limited by volatilization of  $\text{K}_2\text{SiF}_6$ :



A thermogravimetric study showed that the reaction can be detected at about 700°C and volatilization becomes appreciable as the temperature is raised to 750-800°C. Electrodeposition requires that the bath be maintained at constant temperature for several hours and so the highest deposition temperature used was 750°C, the mass of the melt being monitored between experiments. Lithium carbonate normally decomposes at about 1150°C and, although this temperature is reduced substantially by the presence of carbon, the  $\text{Li}_2\text{CO}_3$  was found to be completely stable in the melt at 750°C.

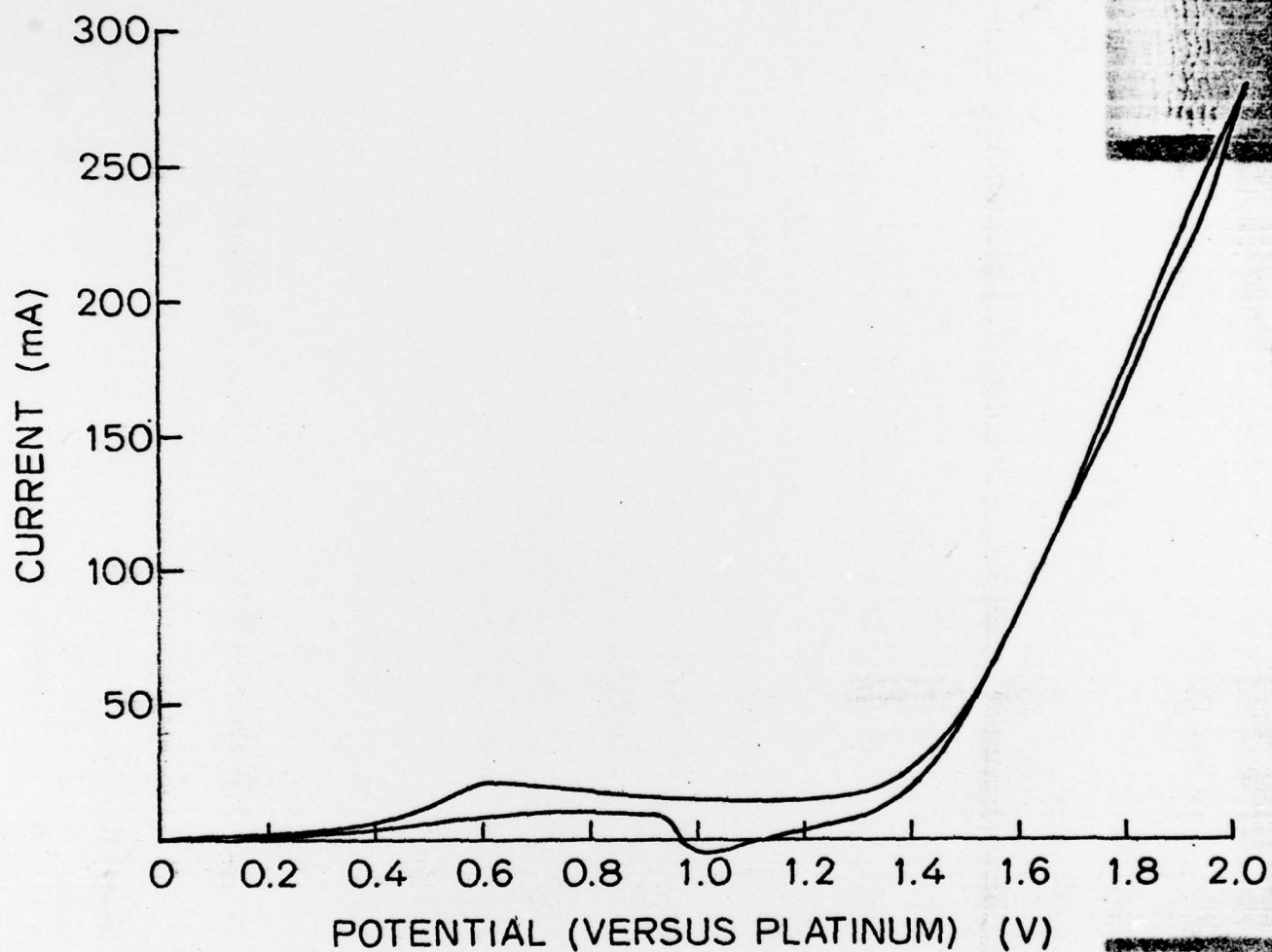


Figure 3. Cyclic voltammogram for composition 0.5 LiF; 0.5 KF; 0.2  $\text{Li}_2\text{CO}_3$ ; 0.05  $\text{K}_2\text{SiF}_6$  (silver cathode).



Identification of SiC in the deposits was mainly based on X-ray diffraction analysis of powders obtained by removing the deposits from the cathode and grinding using an alumina pestle and mortar. If SiC was present, this powdering process would inevitably lead to contamination with alumina. The presence of an appreciable concentration of alumina in the powder is therefore indirect evidence for the formation of SiC since, in the absence of other metallic elements, only the carbide is harder than alumina. However the  $\text{Al}_2\text{O}_3$  diffraction peaks overlap some SiC peaks so that polytype identification is sometimes difficult.

Two experiments, 21 and 38, yielded SiC in the 33R polytype. In both these cases the deposits were made at a fixed potential of 1.60V with a current density around  $30\text{--}40 \text{ mA/cm}^2$ . Increasing the deposition potential, and therefore the current density, resulted in the deposition of lithium silicate  $\text{Li}_2\text{SiO}_3$ , usually in an irregular morphology with high concentrations of trapped LiF. The mechanism by which  $\text{Li}_2\text{SiO}_3$  forms has not been studied but the formation of this material clearly imposes a limitation on the maximum current density which can be used.

The use of potentials below 1.60V normally resulted in no deposit, even with current densities as high as  $30 \text{ mA/cm}^2$ . This absence of a deposit may be associated with the low reactivity of silicon and carbon atoms at a temperature well below the melting point of SiC, the hypothesis being that the SiC deposits but immediately decomposes. Raising the deposition potential to 1.60V increases the driving force for deposition as in the successful experiments, but the use of identical conditions in experiments 45-51 resulted in the deposition of uncombined silicon and carbon. Because of the problem of SiC formation in this system, the emphasis was shifted to an alternative system, the study of which had begun in parallel with the series of experiments described in this section.

#### D. The System $\text{Na}_2\text{CO}_3/\text{NaBO}_2/\text{LiF}/\text{SiO}_2$

The use of borate/carbonate mixtures for the preparation of carbides was introduced by Weiss (1946). He found that electrolysis of  $\text{Li}_2\text{B}_3\text{O}_4/\text{Li}_2\text{CO}_3$  mixtures would yield carbon rather than boron provided that the carbonate/borate ratio was sufficiently high. He also found that the

TABLE II: DEPOSITS FROM SYSTEM  $2\text{NaBO}_2/3\text{Na}_2\text{CO}_3/4\text{LiF}/0.2\text{SiO}_2$  (Continued)

Experiment Number	Cathode	Anode	P.D. (v)	Measurement 2 Density (mA/cm <sup>2</sup> )	Observations
72	SiC	SiC	1.29	122	2H SiC + amorphous carbon
73	SiC	SiC	0.80	5	Small deposit; mainly C
74 <sup>+</sup>	SiC	SiC	0.99	41	$\text{Li}_2\text{SiO}_3$
75*	SiC	SiC	1.24	175	2H SiC + amorphous carbon

Footnotes

- + Increased  $\text{SiO}_2$
- \* Decreased  $\text{Na}_2\text{CO}_3$   
Increased LiF

TABLE II: DEPOSITS FROM SYSTEM  $2\text{NaBO}_2/3\text{Na}_2\text{CO}_3/4\text{LiF}/0.2\text{SiO}_2$ 

Experiment Number	Cathode	Anode	P.D. (v)	Measurement 2 Density (mA/cm <sup>2</sup> )	Observations
50	Ag	Pt	1.50	9	Very little deposit
52	Ag	Ag	1.53	76	Anode dissolved
53	C	C	2.50	178	Probably 21R or 33R SiC + LiF
54	C	C	0.59	12	Very little deposit
55	C	C			Failure
56	C	C	4.99	1840	21R or 33R SiC
57	C	C	0.98	16	No deposit
58	C	C	0.99	28	No deposit
59	SiC	Pt	4.0	2450	Deposit, but no SiC
60	SiC	Pt	1.2	40	No deposit
61	SiC	Pt	1.69	80	Porous deposit, possibly SiC; 10-20% Si with ~50% amorphous C
62	SiC	Pt	1.59	100	Possibly SiC; 5-10% Si + ~50% amorphous C
63	SiC	Pt	1.67	71	Possibly 21R or 33R SiC
64					Test of SiC solubility in melt
65	SiC	C	1.49	80	Small deposit, surface coating
66					Failure
67	SiC	SiC	1.29	77	2H SiC + amorphous carbon
68	SiC	Si			Large battery effect - anode dissolved
69	SiC	SiC	1.30	225	Small deposit; little Si, amorphous C
70	SiC	Pt	1.48	46	Very small deposit; Pt attacked
71	SiC	Pt	1.70	31	Little Si; excess C; Pt attacked



carbides of iron, molybdenum and tungsten could be produced by adding respectively  $\text{Fe}_2\text{O}_3$ ,  $\text{MoO}_3$  or  $\text{WO}_3$  together with an alkali fluoride to lower the melting point and increase the conductivity. The effect of the metaborate addition is still open to speculation but is presumably associated with the formation of a complex within the solution.

The initial composition chosen was based on the experience of preparing these other refractory carbides and the list of experiments performed to date is given in Table 2. Initial experiments with this second system revealed problems with the use both of Pt and Ag as anode materials. Both anode materials dissolved a significant amount, and Pt deposition on the cathode was detected both by microprobe analysis and optical emission spectroscopy. Graphite was tested as an alternative electrode material for both anode and cathode and has been used in some successful depositions (53, 56) as listed in Table 2.

The  $\text{NaBO}_2$  was synthesized initially by reacting to completion  $\text{Na}_2\text{CO}_3$  with  $\text{B}_2\text{O}_3$ . This product was then mixed with further  $\text{Na}_2\text{CO}_3$ , LiF and  $\text{SiO}_2$ , the latter reacting in situ with some carbonate to form sodium silicate.

The success rate with this new melt was much higher than with the earlier system, and the deposition of  $\text{Li}_2\text{SiO}_3$  at high current densities was avoided. Experiments 53 and 56 at high current densities yielded large deposits containing SiC in the 21R or 33R polytype, together with LiF and amorphous carbon, the presence of the latter being indicated both by X-ray diffraction and microprobe analysis. Experiments at lower voltages and current densities failed, however, to yield any deposits.

Silicon carbide was subsequently used as cathode material, in the form of single crystal pieces supplied by Research Organic/Research Inorganic Corporation. These pieces are of the stable 6H polytype, black in color and typically several mm to a few cm in their largest dimension. It was confirmed that their solubility in the melt is negligible at  $750^\circ\text{C}$ . Immediately prior to deposition the crystals were cleaned in an  $\text{HF}/\text{HNO}_3$  solution to remove surface contaminants. The surface of the SiC seed crystals is shown in Fig. 4.

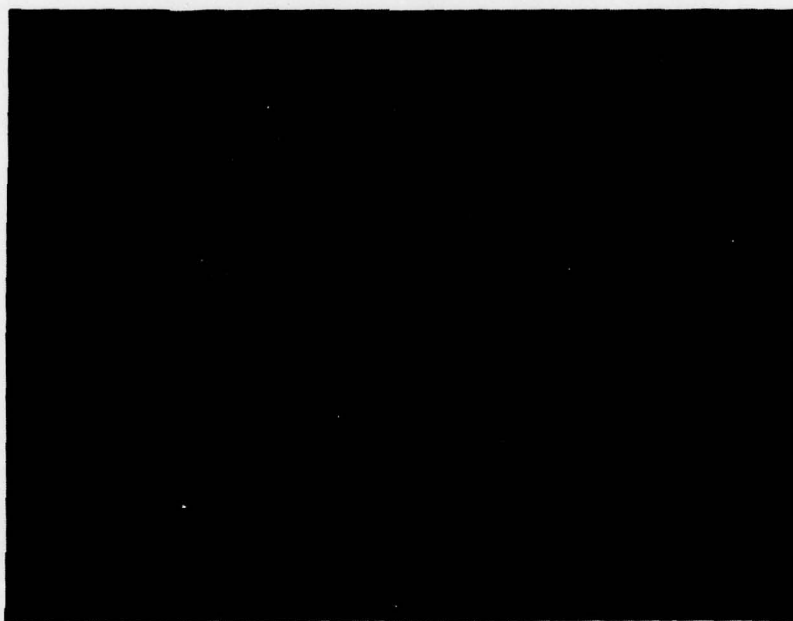


Figure 4. Surface of ROC/RIC SiC crystal  
(200X).

Deposits of SiC were obtained using either Pt or SiC anodes provided that the current density exceeded about  $70 \text{ mA/cm}^2$ . SiC was preferred as an anode material because of the slight attack of the melt on Pt anodes. It was found that the 2H polytype of SiC could be deposited reproducibly at a potential of about 1.3V (experiments 67, 69, 72). These deposits also contain from 50-60 percent of amorphous carbon and some trapped LiF. It was found that the LiF could be removed by dissolution in an  $\text{HF}/\text{HNO}_3$  mixture and that the carbon could be subsequently removed by oxidation. This oxidation was performed at  $760^\circ\text{C}$  in air for 1.5 minutes, the oxidation of SiC being negligible at temperatures below  $800^\circ\text{C}$ . The X-ray diffraction patterns of resulting samples still only showed weak SiC lines (Fig. 5) since the particle size is larger than the ideal. The samples were prepared in a tungsten carbide mortar which permits only impact crushing rather than abrasion, and the mass of material deposited is too small to allow the separation of the finer powder using sieves. It is planned to purchase a boron carbide mortar and pestle to improve powder sample quality.

Figure 6 shows the morphology of SiC (73) deposited on an unpolished ROC/RIC SiC crystal. The deposit is highly polycrystalline and of irregular morphology, this being influenced by the co-deposition of amorphous carbon. The  $\text{SiO}_2:\text{Na}_2\text{CO}_3$  ratio was increased for the two last experiments reported in Table 2 in attempts to reduce or eliminate the excess carbon. In experiment 74 the  $\text{SiO}_2$  concentration exceeded the solubility limit and  $\text{Li}_2\text{SiO}_3$  deposited on the cathode, probably influenced only marginally by the electrodeposition process. Experiment 75 in which the carbonate concentration in the melt was halved and the LiF concentration increased to dissolve more  $\text{SiO}_2$ , 2H-SiC was obtained but excess amorphous carbon was again detected in the deposit. The deposition efficiency was about 8%. Further changes in the melt composition are clearly necessary to reduce the carbonate:silicate ratio.

Figure 7 shows the deposit of experiment 75 after removal from the cathode. The morphology is again irregular but Fig. 7(b) indicates crystalline SiC with up to about  $20 \mu\text{m}$  in size together with amorphous carbon.



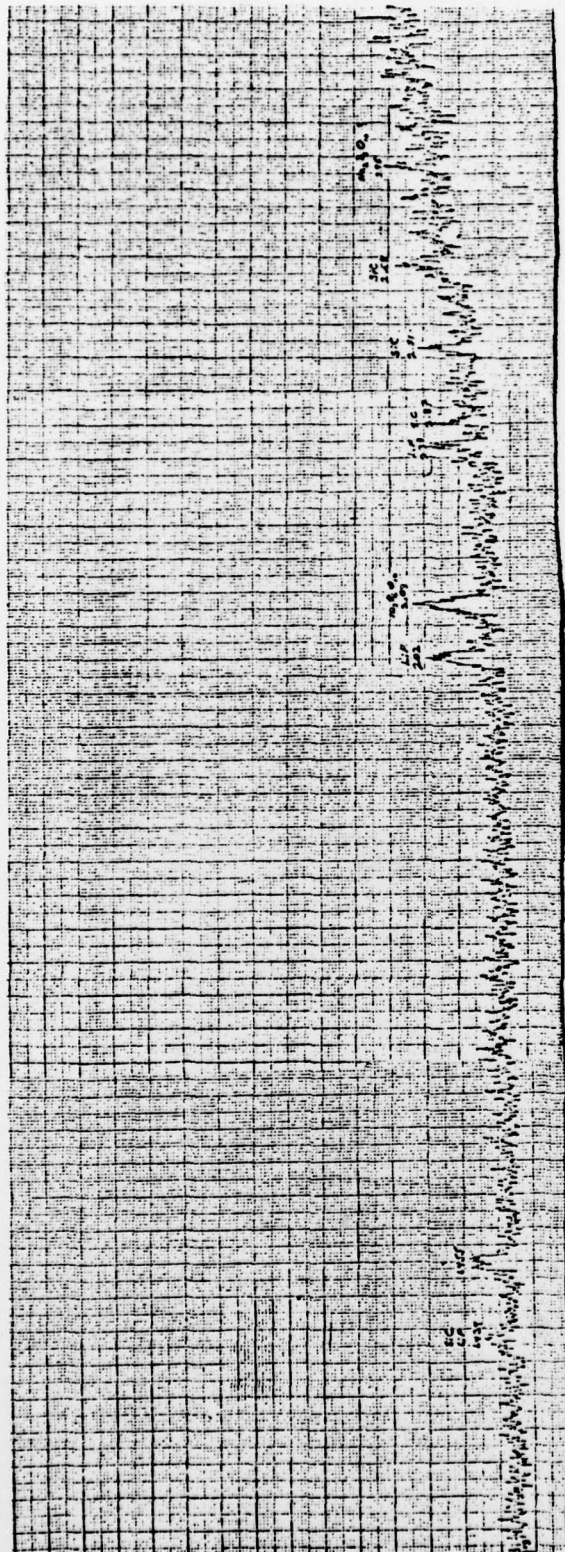


Figure 5. X-ray powder diffraction of deposits from numbers 5, 67, and 72 with identification and d spacing.



Figure 6. SiC deposit on ROC/RIC SiC substrate (200X).

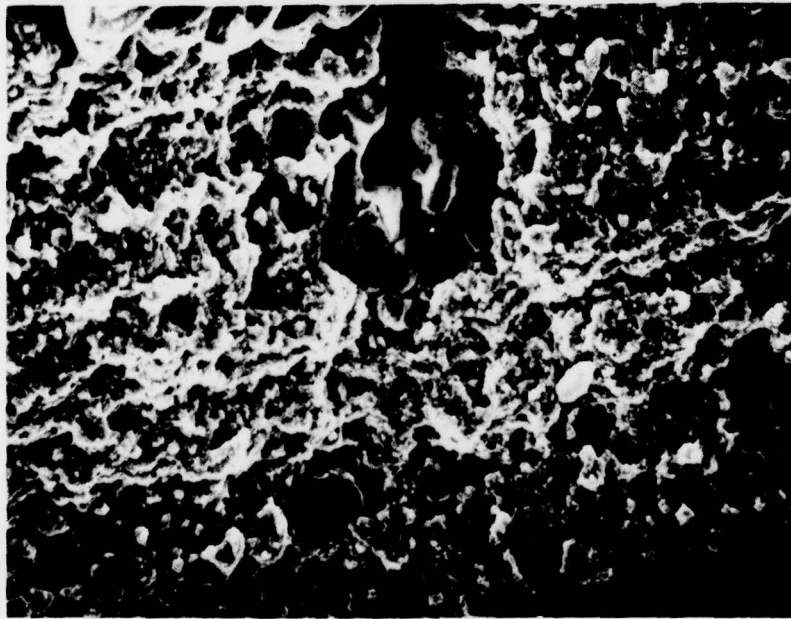
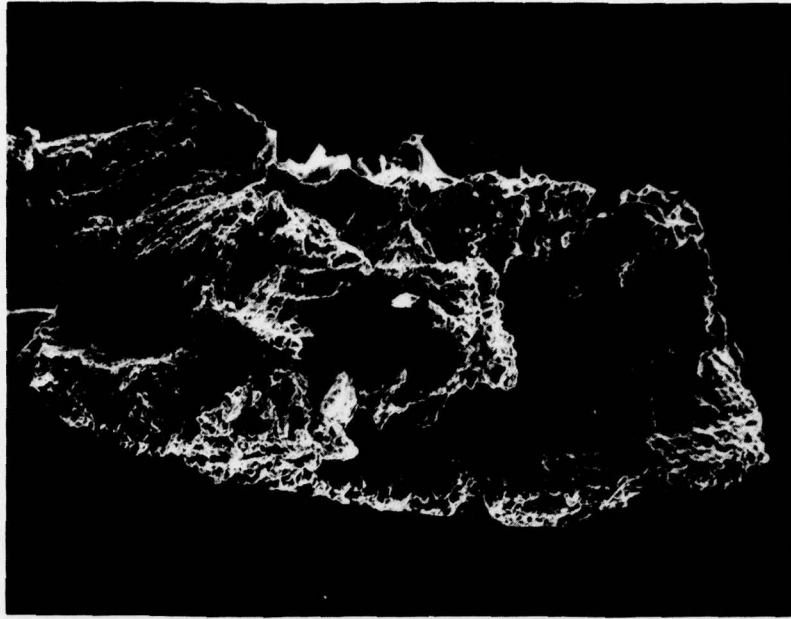


Figure 7(a) SiC deposit removed from SiC  
substrate (60X);  
(b) Microstructure of same deposit  
(200X).



Emission spectrographic analysis of the deposits shows the presence of significant concentrations of boron, chromium, iron, lithium, magnesium and manganese in comparison with the ROC/RIC material. The lithium and boron are probably present as traces of LiF and  $\text{Na}_2\text{BO}_3$  respectively (as suggested by the x-ray data of Fig. 5). The transition metals are almost certainly introduced into the melt by reaction between volatile species from the melt and the inconel atmosphere tube of the furnace. These impurities can therefore be removed by the use of an internally heated furnace which will be introduced into the program during the second year.

#### IV. CONCLUSIONS

The synthesis of silicon carbide by electrodeposition has been achieved for the first time using two different melt compositions. The reproducibility of deposits from the second system, based on that developed by Weiss (1946), is better than that from the  $K_2SiF_6/Li_2CO_3/LiF/KF$  system used earlier. With both systems, it was found difficult to achieve any deposit with potentials close to the minimum deposition potential  $V_a$ , and therefore at low current densities. Since it is normally found (e.g., De Mattei et al., 1978; De Mattei and Feigelson, 1978) that there is a limiting current density for stable deposition of the order of  $10-40 \text{ mA/cm}^2$ , it is to be expected that the requirements of a high current density for SiC electrodeposition will lead to unstable growth and hence to poor morphology.

It seems clear that silicon and carbon combine with difficulty at approximately  $750^\circ\text{C}$  since the individual elements deposit at low current densities. The requirement of a strong driving force for synthesis is consistent with the high melting point of SiC and it is not surprising that the product is the metastable 33R or 2H rather than the stable 6H polytype.

A major emphasis of future work must be to increase the temperature at which deposition occurs since this will facilitate bonding between Si and C atoms. Prior to our study, the lowest temperature at which SiC synthesis had been reported was  $1000^\circ\text{C}$  (Murayama and Takao, 1977), and improved morphology of the electrodeposited material can be expected at temperatures in this region.

A separate problem which must be solved simultaneously is the codeposition with SiC of excess carbon. The factor most likely to affect the Si:C ratio in the deposit is the ratio of silicate to carbonate in the melt and studies of melts of reduced carbonate concentration are already in progress.

A furnace capable of operation at temperatures up to  $1100^\circ\text{C}$  is being used for studies of lithium silicate-carbonate binary melts, and construction of an electrodeposition furnace for  $1500^\circ\text{C}$  is well under way.

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Studies aimed at reducing the impurity content of the deposits are in hand and the 1500°C furnace is expected to give purer deposits than the existing furnaces.

## V. REFERENCES

1. U. Cohen (1977) J. Electronic Materials 6 (1977) 607.
2. R. C. De Mattei, D. Elwell, and R. S. Feigelson (1978), J. Crystal Growth, 44, 545.
3. R. C. De Mattei and R. S. Feigelson (1978) J. Crystal Growth, 44, 115.
4. M. D. Ingram, B. Baron, and G. J. Janz (1965) Rept. # TR-28, RPI-441-35.
5. W. F. Knippenberg (1963) Philips Res. Repts. 18, 161.
6. Y. Murayama and T. Takao (1977) Thin Solid Films, 40, 309.
7. G. M. Rao, D. Elwell, and R. S. Feigelson (1979) Paper presented at AACG/West Conference, Stanford Sierra Camp.
8. Y. M. Tairov, V. F. Tsverkov, M. A. Chernov, and V. A. Taranets (1977), Phys. Stat. Sol (9), 43, 363.

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